DIFFRACTION INVESTIGATIONS OF CEMENT CLINKER AND TRICALCIUM SILICATE USING RIETVELD ANALYSIS

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CERTIFICATE OF AUTHORSHIP / ORIGINALITY

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

Signature of Candidate

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LIST OF ABBREVIATIONS

AINSE	Australian Institute of Nuclear Science and Engineering
AIP	Australian Institute of Physics
ANBF	Australian National Beamline Facility (KEK)
ANSTO	Australian Nuclear Science and Technology Organisation
AM	Alumina Modulus
AMRF	Access to Major Research Facilities
ASRP	Australian Synchrotron Research Program
AXAA	Australian X-ray Analytical Association
BCE	Before Christian Era
BNL	Brookhaven National Laboratories
C_2S	Dicalcium silicate
C_3A	Tricalcium aluminate
C_3S	Tricalcium silicate
C_4AF	Tetracalcium aluminoferrite (brownmillerite)
CTL	Construction Technology Laboratories
C-S-H	Calcium silicate hydrate
DTA	Differential Thermal Analysis
ECM	European Crystallography Meeting
FOM	Figures of Merit
FWHM	Full Width at Half Maximum
GSAS	General Structure Analysis System
GUI	Graphical User Interface
HIFAR	High Flux Australian Reactor
HRPD	High Resolution Powder Diffractometer (HIFAR)
HRTEM	High Resolution Transmission Electron Microscopy
ICCC	International Congress on the Chemistry of Cement
ICNS	International Conference on Neutron Scattering
IUCr	International Union of Crystallography
IMS	Incommensurately Modulated Structures
KEK	High-Energy Accelerator Research Organisation
LSF	Lime Saturation Factor
MPC	Microscope Point Counting

NCNR	National Centre for Neutron Research
NIST	National Institute of Standards and Technology
NSLS	National Synchrotron Light Source
OPC	Ordinary Portland Cement
PCA	Portland Cement Association
PSD	Position Sensitive Detector
QPA	Quantitative Phase Analysis
SAD	Selected Area Diffraction
SCANZ	Society of Crystallography in Australia and New Zealand
SEM	Scanning Electron Microscopy
SOF	Site Occupancy Factor
SR	Silica Modulus
SSC	School on Symmetry of Crystals
SXPD	Synchrotron X-ray Powder Diffraction
TEM	Transmission Electron Microscopy
USA	United States of America
UTS	University of Technology, Sydney
XRD	X-ray Diffraction
XRF	X-ray Fluorescence
XRPD	X-ray Powder Diffraction

ABSTRACT

Cement is the world's most popular building material, yet surprisingly its composition is not fully understood. Due to the complex nature of cement constituents, there is currently no reliable method to quantitatively determine the composition of cement. Partly this arises from the fact that the crystal structure of the main component of cement, tricalcium silicate, has not been fully determined.

There has been an increase in the use of Rietveld refinement of powder diffraction data for the analysis of cement in recent years. The method has emerged as a valuable tool for the quantitative determination of the composition of cement. A further advantage of the method is its ability to refine complex crystal structures, such as tricalcium silicate. Despite the increased application of this method, few publications exist concerning the evaluation or improvement of the method for the purpose of cement analysis.

In this work, the Rietveld method has been critically investigated as a tool for the identification and quantification of the different phases in cement clinker. Laboratory X-ray, synchrotron, neutron, and combined diffraction data are all used in the investigations. For the first time, comparisons of analysis results using various sources are made, rather than comparing the results from various methods. Inconsistencies in the results were found, and their causes were investigated and identified. The reliability of this method was shown to be dependent on the quality of the diffraction data, both in terms of the counting statistics and the resolution, and on the ability of the structures used in the Rietveld model to describe the phases in the sample.

The only previously existing structural model for triclinic tricalcium silicate is shown, in this work, inadequate as a description of the form found in cement. Consequently, the triclinic crystal structures of tricalcium silicate were re-investigated. Using synchrotron powder diffraction data, the lattice dynamics during the T_1–T_2 transition were observed in detail for the first time. Superstructure reflections were observed for the two structures. The first model for the average sub-structure of the T_2 form is presented. Structural modulation in the T_1 form was re-investigated. The parent sub-structure, suitable for Rietveld refinement, corresponding modulation wave-vector, and superspace group of the superstructure, were identified.